

PATENT ABSTRACTS OF JAPAN

(11)Publication number : JP 10-204002

(43)Date of publication of application : 04.08.1998

(51)Int.Cl.

C07B 35/02
B01J 23/58
C07C 5/10
C07C 13/28
C07C 35/21
// C07B 61/00

Kat. Patent

(21)Application number :
09-007468

(71)Applicant :
DAINIPPON INK & CHEM INC
N E CHEMCAT CORP

(22)Date of filing :
20.01.1997

(72)Inventor :
AKIYAMA ATSUYUKI
HASHIMOTO TAKESHI

(54) NUCLEUS HYDROGENATION OF SUBSTITUTED AROMATIC COMPOUND

(57)Abstract:

PROBLEM TO BE SOLVED: To provide nucleus hydrogenation of an aromatic compound that has a high rate of nucleus hydrogenation and is able to selectively control hydrogenation or hydrogenating decomposition of functional groups in a molecular structure.

SOLUTION: This nucleus hydrogenation of an aromatic compound comprises charging a ruthenium catalyst whose carrier, activated carbon, carries ruthenium and sodium atoms, epoxy group-containing aromatic compounds, such as phenylglycidyl ether, and tetrahydrofuran into a reactor vessel, replacing the atmosphere in the vessel with nitrogen, introducing hydrogen under positive pressure, and thereafter carrying out the hydrogenation.

CLAIMS

[Claim(s)]

[Claim 1] The nuclear hydrogenation method of the substitution aromatic compound characterized by supporting the metal atom with electronegativity lower than a ruthenium atom and a ruthenium atom on support, and carrying out nuclear hydrogenation of the substitution aromatic compound under existence of the catalyst whose amount of support of a ruthenium atom is 0.1 - 20%, and hydrogen pressurization.

[Claim 2] The nuclear hydrogenation method according to claim 1 that the amount of support of a metal atom with electronegativity lower than a ruthenium atom is 0.2 - 5%.

[Claim 3] The nuclear hydrogenation method according to claim 1 or 2 that the spectrum peak of Ru3d5/2 orbit when a ruthenium atom measures by the XPS method is the thing of the range of 280.0-281.0eV.

[Claim 4] The nuclear hydrogenation method according to claim 1, 2, or 3 that the low metal atom of electronegativity is alkali metal from a

ruthenium atom.

[Claim 5] The nuclear hydrogenation method according to claim 1, 2, 3, or 4 that support is activated carbon.

[Claim 6] The nuclear hydrogenation method of any one publication of the claim 1-5 which performs nuclear hydrogenation to the bottom of existence of a solvent.

[Claim 7] The nuclear hydrogenation method of any one publication of the claim 1-6 that a substitution aromatic compound is an

aromatic system epoxy resin.

[Claim 8] The nuclear hydrogenation method according to claim 7 that an aromatic system epoxy compound is a bisphenol type epoxy resin.

[Claim 9] The nuclear hydrogenation method according to claim 8 that a bisphenol type epoxy resin is the diglycidyl ether of bisphenol

A, or diglycidyl ether of Bisphenol F.

[Claim 10] The nuclear hydrogenation method of any one publication of the claim 1-9 that a solvent is the alcohol, the shape of a chain,

the cyclic ether, the water, or those mixture of saturation aliphatic series of carbon numbers 1-10.

[Claim 11] The nuclear hydrogenation method according to claim 10 that a solvent is the mixed liquor of a tetrahydrofuran and water.

[Claim 12] The nuclear hydrogenation method of any one publication of the claim 1-11 that hydrogen pressure is 2 - 70 kg/cm², and

reaction temperature is -20-100 degrees C.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] this invention relates to the nuclear hydrogenation method of a substitution aromatic compound of excelling in selectivity and economical efficiency, especially the nuclear hydrogenation method of an aromatic system epoxy resin.

[0002]

[Description of the Prior Art] Generally, in the aromatic compound which has a substituent, hydrogenation of only a nucleus, i.e., nuclear hydrogenation, is very difficult. That is, hydrogenation and hydrocracking of a substituent happened simultaneously in addition to nuclear hydrogenation, and there was a fault of a low in selectivity. And in order to raise [for this reason] the purity of a product in most cases, the complicated refining process was required. Until now, many things are examined about nuclear hydrogenation of the diglycidyl ether of the nuclear hydrogenation method of the aromatic system epoxy resin using the high catalyst of practicality, for example, bisphenol A, for example, the method of carrying out nuclear hydrogenation of the bisphenol A type epoxy resin using a support ruthenium catalyst is mentioned to U.S. JP,3336241,B. Moreover, the method of carrying out nuclear hydrogenation of the bisphenol A type epoxy resin etc. is mentioned to JP,8-53370,A with the ruthenium catalyst which returned using Mg powder.

[0003]

[Problem(s) to be Solved by the Invention] However, by the nuclear hydrogenation method by the ruthenium catalyst which hydrocracking of an epoxy group happens simultaneously, and the method of carrying out nuclear hydrogenation using the support ruthenium catalyst given in U.S. JP,3336241,B has a technical problem called a low in selectivity, and returned it to JP,8-53370,A using Mg powder, the survival rate of an epoxy group had the technical problem that the rate of nuclear hydrogenation fell, although improved.

[0004] While the technical problem which this invention tends to solve can attain the outstanding rate of nuclear hydrogenation which is

not in the former, it is to offer the nuclear hydrogenation method of the aromatic system compound which can suppress hydrogenation and hydrocracking of a substituent for the functional group within the molecular structure alternatively.

[0005]

[Means for Solving the Problem] As a result of inquiring wholeheartedly that this invention person etc. should solve the

above-mentioned technical problem, the low metal atom of electronegativity is supported on support from the ruthenium atom and the ruthenium atom. And the selectivity of very high nuclear hydrogenation was shown to hydrogenation of only a nucleus, i.e., nuclear

hydrogenation, and moreover the catalyst whose amount of support of a ruthenium atom is 0.1 - 20% finds out that this is easily

realizable also in low temperature and low-pressure conditions, and came to complete this invention.

[0006] That is, this invention relates to the nuclear hydrogenation method of the substitution aromatic compound characterized by

supporting the low metal atom of electronegativity on support from the ruthenium atom and the ruthenium atom, and carrying out

nuclear hydrogenation of the substitution aromatic compound under hydrogen pressurization under existence of the catalyst whose

amount of support of a ruthenium atom is 0.1 - 20%, and in a solvent.

[0007] The low metal atom of electronegativity is supported on support from the ruthenium atom and ruthenium atom which are used for

this invention, and the catalyst whose amount of support of a ruthenium atom is 0.1 - 20% Although especially the adjustment method is

not restricted, for example ** ruthenium atom content compound, The compound which contains the low metal atom of electronegativity

from a ruthenium atom is sunk in. After supporting on support with the hardening method, settling, etc., [whether chemical reduction by

reduction processing, for example, the reduction by hydrogen a sodium borohydride, a hydrazine, formic acid, etc. is performed, and] Or

the ruthenium atom content compound which contains the low metal atom of electronegativity from the method of making support on

support, without performing reduction processing, and preparing or ** ruthenium atom is sunk in. After supporting on support with the

hardening method, settling, etc., the method of making support on support, without performing chemical reduction by reduction

processing, for example, the reduction by hydrogen, a sodium borohydride, a hydrazine, formic acid, etc., or performing reduction

processing, and preparing is mentioned.

[0008] here -- as a ruthenium atom content compound -- for example, a ruthenium chloride hydrate and bromination -- a ruthenium

hydrate, a ruthenium oxide hydrate, a chlorination hexa ammine ruthenium, and bromination -- a hexa ammine ruthenium, a

TORINITORATO nitrosyl JIAKUA ruthenium, a tris (acetylacetonato) ruthenium, dodecacarbonyl 3 ruthenium, etc. are raised ** As a

compound which contains the low metal atom of electronegativity from the ruthenium in a method The compound with which

electronegativity contains 2.1 or less metal atom, for example, a potassium, Sodium, caesium, calcium, magnesium, zinc, iron, cobalt, The

hydroxide containing metal atoms, such as nickel and copper, an oxide, an inorganic-acid salt, Organic acid chloride, an organic complex

compound, an inorganic complex compound, etc. are mentioned. Sodium, The hydroxide of alkaline earth metal, such as the hydroxide of

alkali metal, such as a potassium, an oxide, an inorganic-acid salt, organic acid chloride, calcium, and magnesium, an oxide, an

inorganic-acid salt, and organic acid chloride are more desirable, and the hydroxide of alkali metal, an oxide, an inorganic-acid salt, and

organic acid chloride are especially desirable.

[0009] ** As a ruthenium system compound which contains the low metal atom of electronegativity from a ruthenium, the ruthenium

compound which contains sodium and a potassium, for example is mentioned, and ruthenium (VI) acid sodium, ruthenium (VI) acid

potash RIUMU, a PENTAKUROROAKUA ruthenium (III) acid potassium, a PENTA chloro nitrosyl ruthenium (II) acid potassium, an oxy-deca chloro JIRUTENIMU acid potassium, an oxy-deca chloro JIRUTENIMU acid potassium, a fault ruthenium acid potassium, a fault ruthenium acid potassium, etc. are mentioned especially [0010] Although any of an organic system or an inorganic system are sufficient as support as long as it is inactive, for example, it can mention activated carbon, ion exchange resin, a silica, an alpha alumina, gamma-alumina, a silica alumina; a zeolite, various metallic oxides, multiple oxides, etc. to the substituent of the aromatic compound which serves as a raw material of hydrogenation under a reaction condition, the point that the catalyst from which especially a surface area is obtained greatly serves as high activity to its activated carbon is desirable.

[0011] If the manufacture method of the catalyst concerned is explained further in full detail, for example, the matter used as support will be added into water or an organic solvent, and it will consider as 10-100 degrees C. by the method of ** The compound which contains the low metal atom of electronegativity from the ruthenium atom content compound and ruthenium which were mentioned above ** the ** which does not perform reduction processing after adding only the amount corresponding to the target amount of support, infiltrating the ruthenium atom content compound containing the low metal atom of electronegativity from a ruthenium atom, supporting with a method and performing reduction processing -- dryness -- or carry out humidity and prepare As a method in the case of performing reduction processing, after supporting, two methods, A. chemical reduction or B. hydrogen reduction, are mentioned. In the former, after supporting, for example, a reducing agent is added, and it returns, and it filters and washes using water or an organic solvent. By the latter, it filters, for example, it washes using water or an organic solvent, and after drying, it processes at the temperature of -20-550 degrees C under hydrogen atmosphere. And after carrying out reduction processing to the method of A. or B., it considers as dryness or a damp or wet condition. On the other hand, after supporting, it is not necessary to perform reduction processing, and after supporting in that case, filtration and washing are performed and dryness or the method of making carry out humidity and preparing is mentioned.

[0012] The amount of ruthenium support of the catalyst concerned used by this invention is 0.1 - 20% of the weight of a range. At less than 0.1 % of the weight, in order to obtain sufficient rate of nuclear hydrogenation, the large quantity important point of the amount of catalysts is carried out, and the industrial use is difficult. Moreover, in the range exceeding 20 % of the weight, in order that the rate of the ruthenium incorporated in pore may be made to increase in vain and hydrogenation or hydrocracking of a substituent may break out within pore with inadequate diffusion, selectivity falls the bottom.

[0013] The range of 280.0-281.0eV and a bird clapper the supported ruthenium atom It is desirable from the point used as quantity activity. [the spectrum peak of Ru3d5/2 orbit when measuring by the XPS method]

[0014] Although it changes with substitution aromatic series from which the amount of support of the low metallic element of electronegativity is set as the object of hydrogenation from a ruthenium, it is usually 0.2 - 5 % of the weight. It is 0.3 - 2 % of the weight still more preferably. the range exceeding less than 0.2 % of the weight and 5 % of the weight -- hydrogenation of a nucleus -- receiving -- high -- an activity thing is not obtained and both the rate of nuclear hydrogenation and selectivity cannot be satisfied

[0015] The nuclear hydrogenation method of the substitution aromatic compound of this invention is characterized by carrying out nuclear hydrogenation of the substitution aromatic compound under hydrogen pressurization under existence of the catalyst explained

in full detail and in the solvent. Here, each aromatic compound of the monocycle or polycyclic formula which has the substituent which contains various substituents, for example, an alkyl group, or oxygen, nitrogen, and sulfur as a substitution aromatic compound set as the object of hydrogenation can use it, for example, an aromatic carbonyl, an aromatic carboxylic acid, an aromatic alcohol, the aromatic ether, an aromatic epoxy compound, etc. are mentioned. Especially, an aromatic epoxy compound is desirable especially from the point that the usefulness of a catalyst can fully be demonstrated. In addition, although there is especially no limit in the molecular weight of these compounds, the thing of with a molecular weight of 2000 or less molecular weight is desirable.

[0016] As an aromatic epoxy compound which can be used preferably The glycidyl ether of phenols, for example, phenyl glycidyl ether etc.; A bisphenol type epoxy compound, For example, the diglycidyl ether of bisphenol A, the polymerization object of the diglycidyl ether of bisphenol A, and bisphenol A, The polymerization object of the diglycidyl ether of Bisphenol F, the diglycidyl ether of Bisphenol F, and Bisphenol F etc.; A biphenol type epoxy compound, For example, the diglycidyl ether of biphenol, the polymerization object of the diglycidyl ether of biphenol, and biphenol, The diglycidyl ether of 3 and 3', 5', 5'-tetramethyl biphenol, The polymerization object of the diglycidyl ether of 3 and 3', 5', 5'-tetramethyl biphenol, and 3 and 3', 5', 5'-tetramethyl biphenol etc.; A novolak type epoxy compound, For example, although the poly glycidyl ether of a phenol novolak, the poly glycidyl ether of o-cresol novolak, etc. are mentioned, it is not limited to these. Also in these, the point with easy handling as a raw material to a bisphenol type epoxy compound is desirable, and the diglycidyl ether of bisphenol A or the diglycidyl ether of Phenol F is desirable from an especially liquefied point.

[0017] Moreover, usually, although it changes greatly with kinds, reaction conditions, etc. of the amount of support, and the substitution aromatic compound set as the object of hydrogenation, although the amount of said catalyst used is usually suitably chosen from the range of the 0.00005 to 0.5 section to the substitution aromatic compound 1 section, the range of the 0.0001 to 0.2 from a industrial standpoint section is desirable [the amount].

[0018] Although a non-solvent can also perform the hydrogenation reaction of this invention depending on the kind and reaction condition of the substitution aromatic compound set as the object of hydrogenation, it is desirable to carry out in a solvent from the point that improvement in selectivity can be aimed at by selecting the optimal solvent to the reaction made into the purpose, and the point that reaction time can be shortened.

[0019] Although especially the solvent used here is not limited, it can be suitably chosen from a hydrocarbon and ether without a double bond and alcohols, and a halogenated hydrocarbon. As an example, n pentane, n-hexane, a cyclohexane, diethylether, Dibutyl ether, a tetrahydrofuran, a methanol, ethanol, n-propanol, an isopropanol, n-butanol, an isobutanol, 2-butanol, a tert-butanol, n-hexanol, a cyclohexanol, A carbon tetrachloride, a dichloromethane, and trichloroethane are mentioned. especially Diethylether, dibutyl ether, a tetrahydrofuran, a methanol, Ethanol, n-propanol, an isopropanol, n-butanol, an isobutanol, 2-butanol, a tert-butanol, n-hexanol, and a cyclohexanol are desirable, and a tetrahydrofuran is still more desirable.

[0020] The mixture of the alcohol of the saturated-fat group of carbon numbers 1-10, the shape of a chain, cyclic ether, and water is desirable at the point of excelling especially in a reaction rate and a selection system also in these. Water has the effect which raises the activity of a catalyst among said solvents. Therefore, when you need an organic solvent, it is desirable to use as mixed liquor with water as above-mentioned, and the combination of water, ether and water, and alcohols is desirable.

[0021] Although there is especially no limit in the amount of the solvent used when using a solvent, it is weight criteria and the range of the 0.1 to 50 section is preferably desirable the 0.05 to 100 section to the substitution aromatic compound 1 section.

[0022] Although which thing is sufficient as the hydrogen used for the reaction concerned as long as it is usually used industrially, it

becomes the thing excellent in catalytic activity [the direction with few carbon monoxides of an impurity]. Therefore, as for the content

of the carbon monoxide in hydrogen, it is desirable that it is 2% or less. In low voltage, although especially a limit does not have the

hydrogen pressure of reaction time, since a reaction takes the long time more than required and a hydrogen material unit becomes high in

high pressure, the range of 1 - 100 kg/cm² is desirable, and it is desirable to consider as the range of further 2 - 70 kg/cm².

[0023] Although what is necessary is for the reaction temperature in the reaction concerned to change greatly with the kinds, the reaction conditions, and reaction time of the substitution aromatic compound set as the object of hydrogenation, and just to select it suitably in -40-200 degrees C, it improves [the range of -20-100 degrees C is desirable, and / to the substitution aromatic compound

which has an especially reactant high substituent / the range of selectivity of -20-80 degrees C / further] from the point of selectivity and economical efficiency, and is desirable.

[0024] Although the reaction time of the reaction concerned does not generally have ***** depending on the kind, the amount of catalysts, and other reaction conditions of the substitution aromatic compound set as the object of hydrogenation, it is usually 0.5 - 30 hours.

[0025] Like the above, the nucleus hydride easily made into the purpose can be obtained with high selectivity by performing the nuclear hydrogenation reaction of the substitution aromatic compound concerned. Although the point that the process using the ruthenium catalyst concerned is excellent is a point which shows selectivity very high to nuclear hydrogenation, the point that nucleus

hydrogenation can be performed as a point of excelling further, also under the hydrogen pressure force of 2 - 70 kg/cm² and the very

mild conditions of the reaction temperature of -20-100 degrees C is mentioned. Which [whether it considers as the reaction temperature

which considers as the hydrogen pressure force exceeding **100 kg/cm² as conditions for nucleus hydrogenation, or exceeds **100

degree C, and] conditions are required for the ruthenium catalyst generally known. On the other hand, to nuclear hydrogenation, since

activity is very high, the catalyst concerned can make previous conditions possible and can make them a very cheap manufacturing cost and facility cost.

[0026] In addition, the ruthenium catalyst concerned can be acquired very cheaply. Furthermore, since it is also possible to use it

repeatedly, the nuclear hydrogenation method concerned is an advantageous method also at the point that catalyst cost can be held down.

[0027] In addition, as long as it bears the hydrogen pressure needed as a reaction facility, there may be no limit and which method of a

batch process and continuous system may be used for it. Although what removed only the solvent can be made into the specified

substance with high purity after removing a catalyst by filtration etc., the nucleus hydride obtained by this invention can also be refined

using the method that distillation, crystallization, etc. are conventionally better known still, if required.

[0028] According to the nuclear hydrogenation method using the catalyst concerned, nuclear hydrogenation of a substitution aromatic

compound, for example, an aromatic system epoxy compound etc., can be performed to high selection, and can be performed economically.

[0029]

[Example] Although an example is given to below and this invention is further explained to it at a detail, this invention is not limited to these. In addition, unless it mentioned specially below, it asked for the rate of nuclear hydrogenation from analysis of an ultraviolet spectrum, and asked for the epoxy-group survival rate from the measurement result of a weight per epoxy equivalent.

[0030] The example 1 (the catalyst manufacture method) of reference

Added 10.0g of activated carbon, and 100g of water to the 200ml beaker, it was made to sink in, agitating, after adding the ruthenium (VI)

acid sodium solution which does % content of 0.5g for a ruthenium atom at a room temperature, and it dehydrated, after filtering this and

washing it by ion exchange water. The acquired catalyst was 50 % of the weight of water contents, and the amount of support of a

ruthenium atom and the amount of support of a sodium atom were 5 % of the weight per dry weight, and 1 % of the weight respectively.

Moreover, the spectrum peak of Ru3d5/2 orbit when measuring the supported ruthenium atom by the XPS method was a 280.7eV thing.

[0031] 2g [of ruthenium catalysts prepared in the example 1 to the autoclave reactor of 11l. of examples] (50-% of the weight water), and

phenyl-glycidyl-ether (weight per epoxy equivalent 150) 30g, and tetrahydrofuran 80g. After nitrogen gas's replacing the gas in

preparation and a reactor and setting it as 80 degrees C, in addition, hydrogen is sealed so that the pressure in a reactor may serve as 40

kg/cm², and it was made to react for 1 hour until pressure reduction of hydrogen was completed. When the catalyst was filtered after the

reaction end and the gas chromatography analyzed the obtained filtrate, 100% of rates of nuclear hydrogenation was checked, and the

selectivity of cyclohexyl glycidyl ether was 98%. Subsequently, the evaporator removed the solvent. Although obtained, the weight per epoxy equivalent was 159.

[0032] The example 2 (the catalyst manufacture method) of reference

Add 10.0g of activated carbon, and 100g of water to a 200ml beaker, and it is made to sink in, agitating, after adding the ruthenium (VI)

acid sodium solution which does % content of 0.5g for a ruthenium at a room temperature, and filters, and after washing by ion exchange

water and dehydrating, it heated for 2 hours and was made to return at 80 degrees C under hydrogen atmosphere. The amount of support

of a ruthenium and the amount of support of sodium of the acquired catalyst were 5 % of the weight per dry weight, and 1 % of the

weight respectively. Moreover, supported ruthenium atom The spectrum peak of Ru3d5/2 orbit when measuring by the XPS method was

a 280.4eV thing.

[0033] 1g [of ruthenium catalysts prepared in the example 3 to the autoclave reactor of 21l. of examples] (dryness article), and

phenyl-glycidyl-ether (weight per epoxy equivalent 150) 30g, and tetrahydrofuran 80g. After nitrogen gas's replacing the gas in

preparation and a reactor and setting it as 80 degrees C, in addition, hydrogen is sealed so that the pressure in a reactor may serve as 40

kg/cm², and it was made to react for 1 hour until pressure reduction of hydrogen was completed. When the catalyst was filtered after the

reaction end and the gas chromatography analyzed the obtained filtrate, 100% of rates of nuclear hydrogenation was checked, and the

selectivity of cyclohexyl glycidyl ether was 97%. Subsequently, the evaporator removed the solvent. Although obtained, the weight per epoxy equivalent was 161.

[0034] EPICLON850CRP(weight-per-epoxy-equivalent 173, Dainippon Ink & Chemicals, Inc. make) 30g, 10g of water, and tetrahydrofuran

80g that is 4g (50-% of the weight water) of ruthenium catalysts and the diglycidyl ether of bisphenol A which were prepared in the

example 1 to the autoclave reactor of 31l. of examples. After nitrogen gas's replacing the gas in preparation and a reactor and setting it as

40 degrees C, in addition, hydrogen is sealed so that the pressure in a reactor may serve as 40 kg/cm², and it was made to react for 7

hours until pressure reduction of hydrogen was completed. The catalyst was filtered after the reaction end and 150mmHg(s) removed the solvent at 150 degrees C. The rate of nuclear hydrogenation was 100%, and although obtained, the weight per epoxy equivalent was 189, and the epoxy-group survival rate was 96%.

[0035] It reacted on the same conditions as an example 3 except having considered as reaction-time 9 hours using 5% activated carbon support ruthenium (50-% of the weight water) 4g of marketing as example of comparison 1 catalyst. The catalyst was filtered after the reaction end and 150mmHg(s) removed the solvent at 150 degrees C. The rate of nuclear hydrogenation was 67%, and although

obtained, the weight per epoxy equivalent was 228, and the epoxy-group survival rate was 77%.

[0036] It reacted on the same conditions as an example 3 except having made the reaction temperature of 50 degrees C, and the

introductory pressure of hydrogen into 100 kg/cm² using 5% activated carbon support ruthenium (dryness article) 6g of marketing as

example of comparison 2 catalyst, using dioxane 240g as a solvent, and having considered as reaction-time 24 hours. The catalyst was

filtered after the reaction and 150mmHg(s) removed the solvent at 150 degrees C. The rate of nuclear hydrogenation was 81%, and

although obtained, the weight per epoxy equivalent was 29, and the epoxy-group survival rate was 67%.

[0037] It reacted on the same conditions as the example 1 of comparison except having considered as example of comparison 3 reaction

temperature [of 80 degrees C], and reaction-time 6 hours. The catalyst was filtered and 150mmHg(s) removed the solvent at 150 degrees

C. The rate of nuclear hydrogenation was 82%, and although obtained, the weight per epoxy equivalent was 254, and the epoxy-group survival rate was 69%.

[0038] It reacted on the same conditions as the example 1 of comparison except having made 5% activated carbon support rhodium (50-%

of the weight water) 2g of example of comparison 4 marketing into the catalyst, and having considered as reaction-time 5 hours. The

catalyst was filtered after the reaction end and 150mmHg(s) removed the solvent at 150 degrees C. The rate of nuclear hydrogenation

was 100%, and although obtained, the weight per epoxy equivalent was 242, and the epoxy-group survival rate was 81%.

[0039] It reacted on the same conditions as an example 3 except having used EPICLON850 (weight-per-epoxy-equivalent 189, Dainippon

Ink & Chemicals, Inc. make) 30g which is diglycidyl ether of bisphenol A as example 4 raw material. The catalyst was filtered after the

reaction end and 150mmHg(s) removed the solvent at 150 degrees C. The rate of nuclear hydrogenation was 100%, and although

obtained, the weight per epoxy equivalent was 206, and the epoxy-group survival rate was 95%.

[0040] It reacted on the same conditions as an example 3 except having used EPICLON830 (weight-per-epoxy-equivalent 180, Dainippon

Ink & Chemicals, Inc. make) 30g which is diglycidyl ether of Bisphenol F as example 5 raw material. The catalyst was filtered after the

reaction end and 150mmHg(s) removed the solvent at 150 degrees C. The rate of nuclear hydrogenation was 100%, and although

obtained, the weight per epoxy equivalent was 198, and the epoxy-group survival rate was 95%.

[0041] 24.4g [of ruthenium chloride hydrates.] and tetrahydrofuran 1000g was taught, and it considered as nitrogen atmosphere, and it

heated in the 4 mouth flask of 52l. of examples of comparison, having added 75g of magnesium dusts and agitating for 5 hours, and,

subsequently was made it the ** exception.

[0042] 12.9g of solutions of the catalyst acquired by the 11. autoclave reactor, After teaching EPICLON830 (weight-per-epoxy-equivalent

180, Dainippon Ink & Chemicals, Inc. make) 30g and tetrahydrofuran 20g which is diglycidyl ether of Bisphenol F, and nitrogen gas's

replacing the gas in a reactor and setting it as 50-70 degrees C, in addition, hydrogen is sealed so that the pressure in a reactor may serve as 100 kg/cm², and it was made to react for 12 hours until pressure reduction of hydrogen was completed. The catalyst was filtered after the reaction end and 150mmHg(s) removed the solvent at 150 degrees C. The rate of nuclear hydrogenation was 90%, and although obtained, the weight per epoxy equivalent was 200, and the epoxy-group survival rate was 93%. an example 5 -- comparing -- a high pressure -- ** -- in spite of having carried out and having lengthened reaction time, the rate of nuclear hydrogenation brought a low result

[0043] As 6g (50-% of the weight water) of ruthenium catalysts and the raw material which were prepared in the example 1 to the autoclave of 611. of examples. After teaching EPICLON1055 (weight-per-epoxy-equivalent 498, Dainippon Ink & Chemicals, Inc. make) 30g, 20g [of water], and tetrahydrofuran 120g which is the polycondensation object of the diglycidyl ether of bisphenol A, and nitrogen gas's replacing the gas in a reaction container and setting it as 50 degrees C, in addition, it seals so that the hydrogen pressure force may serve as 40 kg/cm², and it was made to react for 12 hours until pressure reduction of hydrogen was completed. The catalyst was filtered after the reaction end and 150mmHg(s) removed the solvent at 150 degrees C. The rate of nuclear hydrogenation was 96%, and although obtained, the weight per epoxy equivalent was 568, and the epoxy-group survival rate was 91%.

[0044] It reacted on the same conditions as an example 6 using EPICLON4055 (weight-per-epoxy-equivalent 917, Dainippon Ink & Chemicals, Inc. make) 30g which is the polycondensation object of the diglycidyl ether of bisphenol A as example 7 raw material except having considered as reaction-time 16 hours. 150mmHg(s) removed the solvent at 150 degrees C after the reaction end. The rate of nuclear hydrogenation was 92%, and although obtained, the weight per epoxy equivalent was 1070, and the epoxy-group survival rate was 89%.

[0045] 30g of bisphenol A was used as example 8 raw material, t-butanol 80g was used as a solvent, and it reacted on the same conditions as an example 2 except having considered as reaction-time 3 hours. When the catalyst was filtered after the reaction end and the gas chromatography analyzed the obtained filtrate, the selectivity of the screw (4-hydronalium cyclohexyl) propane which 100% of rates of nuclear hydrogenation is checked, and consists of three sorts of isomers was 99%.

[0046]

[Effect of the Invention] While the outstanding rate of nuclear hydrogenation which is not in the former can be attained according to this invention, the nuclear hydrogenation method of the aromatic system compound which can suppress hydrogenation and hydrocracking of a substituent for the functional group within the molecular structure alternatively can be offered.

[0047] moreover, a nuclear hydrogenation reaction -- low temperature -- low -- since it can carry out under pressure conditions, productivity also improves

[Translation done.]